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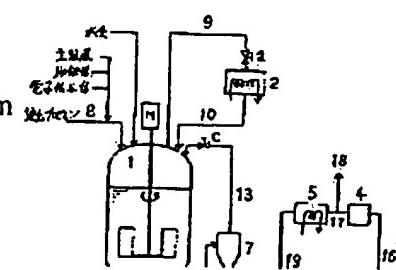
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(54) CONTINUOUS PRODUCTION OF POLYOLEFIN

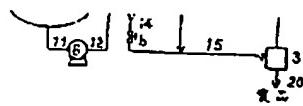
(57)Abstract:

PURPOSE: To produce a polyolefin continuously in high productivity and high catalyst availability by withdrawing a slurry having a concentration higher than that in the polymerizer and containing polyolefin particles having a larger particle diameter from the polymerizer.

CONSTITUTION: This process is one for performing the slurry or bulk polymerization of an olefinic monomer, wherein for example liquefied propylene is fed into a polymerizer 1 through a line 8, a



stereoregular polymerization catalyst such as a Ziegler/Natta catalyst as the main catalyst, a promoter and an electron donor are fed continuously into the line 8 in its middle, the liquefied propylene is polymerized in the polymerizer 1 to form polypropylene particles including the active catalyst and slurried in the liquefied propylene, this slurry is withdrawn from a line 11 and treated in a cyclone 7 to separate the larger particles, the smaller particles remaining in the slurry are returned to the polymerizer 1 through a line 13, and the larger particles are sent to a solid-gas separator 3 through a line 15, separated from the liquefied propylene, withdrawn from a line 20 and recovered as a product.



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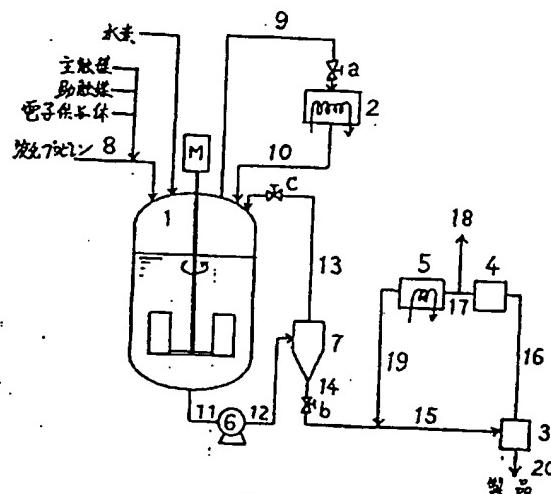
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(57) 【要約】

【構成】プロピレン等をスラリー重合又はバルク重合してポリプロピレンを製造するプロセスにおいて、重合槽内のスラリーを連続的に抜き出し、スラリー中のポリプロピレン粒子をサイクロン等で連続的に分級し、径の小さなポリプロピレン粒子のスラリーのみを重合槽内に戻し、径の大きなポリプロピレン粒子のスラリーを製品として回収する。

【効果】重合触媒の利用効率が向上し、プロピレンの仕込み量に対するポリプロピレンの収率が高まる。



【特許請求の範囲】

【請求項1】1又は2以上の重合槽を用いて、立体規則性触媒によってオレフィン系モノマーをスラリー重合又はバルク重合してポリオレフィンを製造するプロセスにおいて、(a)重合槽内のスラリーを連続的に抜き出し、(b)抜き出したスラリー中のポリオレフィン粒子を連続的に分級し、重合槽内のスラリー濃度よりも高いスラリー濃度を有し、且つスラリー中のポリオレフィン粒子が主に粒径の大きなものから構成されるところのスラリーを得、(c)このスラリーを重合槽外に取り出し、重合槽から抜き出したスラリーの残りの部分を当該重合槽に戻す、ことを特徴とするポリオレフィンの連続製造プロセス

[Name] Yamagata Kenji

(57) [Abstract]

[Constitution] Slurry polymerization or bulk polymerization doing propylene, etc slurry inside polymerization vessel in continuousthe classification it does polypropylene particle in slurry in continuous with such as extractand cyclone in process which produces polypropylene, resets only slurryof small polypropylene particle of diameter into polymerization vessel, it recovers with theslurry of big polypropylene particle of diameter as product.

[Effect(s)] Use efficiency of polymerization catalyst improves, yield of polypropylene for input amountof propylene increases.

[Claim(s)]

[Claim 1] Polymerization vessel of 1, 2 or more using, With stereoregular catalyst olefin monomer slurry polymerization to do, Or bulk polymerization doing, In process which produces polyolefin , slurry inside (a) polymerization vessel in continuous extract, (b) polyolefin particle in slurry which is extracted in continuous classification todo, It possesses slurry concentration which is higher than slurry concentration inside the polymerization vessel, it obtains slurry of place where at same time thepolyolefin particle in slurry is formed mainly from big ones of particle diameter, (c)removes this slurry outside polymerization system, it designates that remainingportion of slurry which is extracted from polymerization vessel is reset to thethis said polymerization vessel as feature, continuous production process of polyolefin

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、1の重合槽又は2以上の直列に接続した重合槽中で、チーグラー・ナッタ触媒等の立体規則性触媒によってオレフィン系のモノマーを連続的に重合するポリオレフィンの連続製造プロセスの改良に関する。

【0002】

【従来の技術】高密度ポリエチレン、線状低密度ポリエチレン、ポリプロピレン、エチレン・プロピレン共重合体、エチレン・プロピレンゴム、エチレン・プロピレン・ジエン共重合体等のポリオレフィンは、チーグラー・ナッタ触媒等の立体規則性触媒を用いて、単独の重合槽或いは2以上の直列に接続した重合槽中で、スラリー重合やバルク重合等のプロセスにより、連続的に製造されることが多い。これらのプロセスにおいては、ポリオレフィンは、内部に触媒を包含した粒子として回収される。

【0003】スラリー重合やバルク重合において、モノマー供給量に対する転化率を高めるため、重合槽中のスラリー濃度を高めることが検討された。しかし、スラリー重合やバルク重合において重合槽中のスラリー濃度を余り高くすると、攪拌が困難となり均一な重合が困難になるという問題があることはこれまで知られていた。例えば、スラリー重合によるプロピレンの重合においては、スラリー濃度は35重量%が安定運転のできる限界であるといわれていた。一方、バルク重合においては50重量%程度が安定運転の限界と言われていた。

【0004】従来、バルク重合においては、重合槽内のスラリーは重合槽に設けた抜き出しラインから断続的に抜き出していた。これは、重合槽の内部が20~60kg/cm²Gの高圧である一方、抜き出しライン内部は1~10kg/cm²G程度の低圧であるからである。このように断続的にスラリーを抜き出すことにより、重合槽の内圧を保つとともに、バルブの開閉タイミングを制御することによりスラリーの抜き出し量を制御していた。

【0005】

【解決すべき課題】従来は、このように重合槽内のスラリー

[Description of the Invention]

[0001]

[Field of Industrial Application] This invention in polymerization vessel which is connected to polymerization vessel of 1 or the series array of 2 or more, polymerizes monomer of olefin to the continuous with Ziegler-Natta catalyst or other stereoregular catalyst, it regards improvement of continuous production process of the polyolefin.

[0002]

[Prior Art] As for high density polyethylene, linear low density polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-propylene rubber and the ethylene * propylene * diene copolymer or other polyolefin, in polymerization vessel which is connected to polymerization vessel of alone or the series array of 2 or more making use of Ziegler-Natta catalyst or other stereoregular catalyst, there is many a thing which is produced in continuous by slurry polymerization and bulk polymerization or other process. Regarding these process, polyolefin recovers as particle which includes the catalyst in inside.

[0003] In slurry polymerization and bulk polymerization, in order to raise conversion ratio for monomer supplied amount, raising slurry concentration in polymerization vessel was examined. But, when slurry concentration in polymerization vessel is made excessively high in slurry polymerization and bulk polymerization, churning becomes difficult and it was known so far that it is problem that uniform polymerization becomes difficult. At time of polymerizing propylene with for example slurry polymerization, as for slurry concentration it was said that it is a limit which stable operation can do 35 weight %. On one hand, 50 weight % extent was called limit of stable operation regarding the bulk polymerization.

[0004] Until recently, it extracted slurry inside polymerization vessel from removal line which is provided in polymerization vessel in discontinuous regarding bulk polymerization. Because as for this, although inside of polymerization vessel is high pressure of the 20 to 60 kg/cm²G as for removal line inside it is a low pressure of 1 to 10 kg/cm²G extent. This way as internal pressure of polymerization vessel is maintained by extracting the slurry in discontinuous, withdrawn amount of slurry was controlled by controlling opening and closing timing of valve.

[0005]

[Problem to be solved] Until recently, this way because slurry in

を単にそのまま断続的に抜き出していたに過ぎなかつたので、重合槽中のスラリー濃度が、そのままモノマー供給量当たりのポリオレフィン粒子への転化率となり、モノマー供給量当たりのポリオレフィン粒子への転化率は上記の制限を超えることができなかつた。又、抜き出されたスラリーには、粒径の小さなポリオレフィン粒子も大量に含まれていた。これらの粒径の小さなポリオレフィン粒子は未だ重合が余り進行しておらず、粒子中の触媒の活性点密度が高く且つ活性が未だかなり高い。従つて、未だ活性の高い触媒がポリオレフィン粒子に含まれた形でショートパスすることになるので、触媒の利用効率が低くなり、生産性が低下するという問題があつた。

【0006】又、活性点密度の高い、即ち滞留時間の短い粒径の小さなポリオレフィン粒子が製品に混入するので、フィルムグレードにおいてはフィッシュアイが生じやすくなり、射出成形グレードにおいては耐衝撃強度の高い成形品が得られず、又、成形品に表面荒れが生じやすいという問題があつた。

【0007】更に、抜き出しラインからは、上にも述べたように重合槽内のスラリーをそのまま抜き出すので、ポリオレフィン粒子とともに大量のモノマーも抜き出されることとなる。このため、回収すべきモノマー量が多くなる結果、モノマー回収設備が大型化し、モノマー回収に要するエネルギーが多くなるという問題があつた。本発明は、従来のスラリー重合やバルク重合等のプロセスにおける生産性及び触媒利用効率の改善を目的とする。

【0008】

【課題解決のための手段】本発明は、1又は2以上の重合槽を用いて、立体規則性触媒によってオレフィン系モノマーをスラリー重合し又はバルク重合しポリオレフィンを製造するプロセスにおいて、(a)各重合槽において当該重合槽内のスラリーを連続的に抜き出し、(b)抜き出したスラリーを連続的に分級し、スラリー濃度が重合槽内のスラリー濃度よりも高く且つスラリー中のポリオレフィン粒子が主に粒径の大きなものから構成されるところのスラリーを得、(c)このスラリーを重合系外に取り出し、重合槽から取り出したスラリーの残りの部分を当該重合槽に戻す、ことを特徴とするものに関する。

【0009】本発明の連続製造プロセスは、各種ポリオレフ

side polymerization vessel only was extracted simply that way discontinuous, slurry concentration in polymerization vessel, became the conversion ratio to polyolefin particle of per amount of monomer supplied that way, as for conversion ratio to the polyolefin particle of per amount of monomer supplied it was not possible to exceed above-mentioned restriction. also, also small polyolefin particle of particle diameter was included in large scale in slurry which is extracted. As for polyolefin particle where these particle diameter are small yet polymerization is not excessively advancing, active site density of catalyst in particle to be high and activity still is quite high. Therefore, because in form where catalyst where still activity is high is included in polyolefin particle it means short path to do, use efficiency of catalyst becomes low, there was a problem that productivity decreases.

[0006] Also, active site density it is high, because namely small polyolefin particle of particle diameter where residence time is short mixes to product, fisheye becomes easy to occur regarding film grade, molded article where impact resistance is high regarding the injection molding grade is not acquired, there was a problem that surface roughening is easy to occur in also, molded article.

[0007] Furthermore, because, as expressed even on, slurry inside polymerization vessel is extracted that way from removal line, with polyolefin particle it means with that also monomer of large scale is extracted. Because of this, result and monomer recovery facility where monomer amount which should recover becomes many do scale-up. there was a problem that the energy which is required in monomer recovery becomes many. As for this invention, improvement of productivity and catalyst utilization efficiency in conventional slurry polymerization and bulk polymerization or other process is designated as object.

【0008】

【Means for problem solving】As for this invention, polymerization vessel of 1, 2 or more using, With stereoregular catalyst olefin monomer slurry polymerization to do, Or bulk polymerization to do, In process which produces polyolefin putting, (a) In each polymerization vessel slurry inside this said polymerization vessel in continuous extract, (b) slurry which is extracted classification is done in continuous, the slurry concentration is higher than slurry concentration inside polymerization vessel, you obtain slurry where at same time polyolefin particle in slurry is formed mainly from big ones of particle diameter, (c) remove this slurry outside polymerization system, you regard those which designate that remaining portion of slurry which is removed from polymerization vessel is reset to this said polymerization vessel as feature.

[0009] It can apply to production of various polyolefin continu-

インの製造に適用できる。具体的には、高密度ポリエチレン、線状低密度ポリエチレン、ポリプロピレン、エチレン・プロピレン共重合体、エチレン・プロピレンゴム、エチレン・プロピレン・ジエン共重合体等のポリオレフィンの製造に適用できる。

[0010] このプロセスで用い得るオレフィン系モノマーとしては炭素数2～8の α -オレフィンが挙げられる。具体的にはエチレン、プロピレン、1-ブテン、1-ペンテン、4-メチルペンテン-1、1-ヘキセン、1-オクテンからなる群から選ばれる1種又は2種以上の α -オレフィンがある。

[0011] 用い得る触媒としては、立体規則性触媒が挙げられる。具体的には、 $TiCl_4-AlR_3$ 系(R はアルキル基)触媒や、 $TiCl_4-AlR_2X$ (X はハロゲン)系触媒、或いはこれらを塩化マグネシウムや水酸化マグネシウムに担持した触媒、或いは、 $TiCl_4-AlR_3$ 系触媒や、 $TiCl_4-AlR_2X$ 系触媒をマグネシウムアルコキシドと反応させたもの等のポリエチレン製造用チーグラー・ナッタ触媒、 $TiCl_3-AlR_2X$ 系触媒等の第1世代チーグラー・ナッタ触媒、所謂Solvay触媒等の第2世代チーグラー・ナッタ触媒、内部ドナーとしてフタル酸ジエステル等を含んだハロゲン化マグネシウムにハロゲン化チタンを担持させた担持型固体触媒と有機Al化合物と各種シラン化合物等の外部ドナーとを組み合わせて調製した第3世代チーグラー・ナッタ触媒等のポリプロピレン製造用チーグラー・ナッタ触媒が挙げられる。更に、 VOC_3 や VCl_4 等のV化合物とエチルアルミニウムセスキクロライド等の有機Al化合物を主要成分とするエチレン・プロピレンゴム製造用触媒、及び各種カミンスキ触媒等も好ましく用いられる。

[0012] 本発明の連続製造プロセスを適用し得る重合プロセスとしては、単独の重合槽、又は直列に接続した2以上の重合槽を用いた連続重合法が挙げられ、具体的には、スラリー重合及びバルク重合等に好ましく適用できる。ここでスラリー重合とは、オレフィン系モノマーは溶解するが生成したポリオレフィンは溶解しない溶媒中で重合を行なうプロセスをいう。一方、バルク重合は、オレフィン系モノマー中で重合を行なうプロセスをいう。

[0013] 本発明の連続製造プロセスにおいては、ポリオレフィン粒子を未反応モノマーや溶媒とともに重合槽からスラリーとして抜き出し、このスラリー中のポリオレフィン粒子を粒径の大きなものと小さなものに分ける。そして粒径の小さなポリオレフィン粒子は、未反応モノマーや溶媒の大部分とともに重合槽に戻される。一方、粒径の大きなポリオレ

ous production process of the this invention. Concretely, it can apply to production of high density polyethylene, linear low density polyethylene, the polypropylene, ethylene-propylene copolymer, ethylene-propylene rubber and ethylene * propylene * diene copolymer or other polyolefin.

[0010] You can list carbon number 2 to 8 -olefin monomer which it can use with this process. There is a -olefin of one, two or more kinds which concretely is chosen from the group which consists of ethylene, propylene, 1-butene, 1-pentene, the 4-methylpentene-1, 1-hexene and 1-octene.

[0011] You can list stereoregular catalyst using as catalyst which is obtained. Concrete, $TiCl_4-AlR_3$ (As for R alkyl group) catalyst and $TiCl_4-AlR_2X$ (As for X halogen)-based catalyst. Or these catalyst which is borne in magnesium chloride and magnesium hydroxide. Or, $TiCl_4-AlR_3$ -based catalyst and $TiCl_4-AlR_2X$ -based catalyst Ziegler-Natta catalyst for thing or other polyethylene structure which reacts with themagnesium alkoxide. $TiCl_3-AlR_2X$ -based catalyst or other 1st generation Ziegler-Natta catalyst and generally known Solvay catalyst or other second generation Ziegler-Natta catalyst. You can list Ziegler-Natta catalyst for 3rd generation Ziegler-Natta catalyst or other polypropylene production which is manufactured combiningwith carrier type solid catalyst and organic Al compound and various silane compound or other external donor which bear titanium halide in the magnesium halide which includes phthalic acid diester etc as internal donor. Furthermore, catalyst for ethylene-propylene rubber manufacture which designates VOC_3 and the VCl_4 or other V compound and ethyl aluminum sesquichloride or other organic Al compound as main component, also various Kaminsky catalystetc are desirably used.

[0012] You can list continuous polymerization method which uses polymerization vessel of 2 or more which is connected to polymerization vessel, or series array of alone as polymerization process which can apply continuous production process of this invention, concretely, can apply to slurry polymerization and bulk polymerization etc desirably. slurry polymerization, it melts olefin monomer here, but polyolefin which is formed is the process which polymerizes in solvent which is not melted. On one hand, bulk polymerization is process which polymerizes in olefin monomer.

[0013] Regarding continuous production process of this invention, polyolefin particle in extract and this slurry big ones of particle diameter is divided into small ones with unreacted monomer and solvent polyolefin particle as slurry from polymerization vessel. And small polyolefin particle of particle diameter with major portion of unreacted monomer and

フィン粒子は、未反応モノマーや溶媒の一部分とともにスラリーとして重合系外に取り出される。この重合系外に取り出されるスラリーを以下「濃縮スラリー」ということとする。濃縮スラリーのスラリー濃度は、重合槽内のスラリー中のそれよりも大きいことが必要であるが、スラリー濃度が75重量%を超えると、濃縮スラリーの流動性が低くなり、重合系外に円滑に取り出すことができなくなるから好ましくない。特に好ましいスラリー濃度は70重量%以下である。

[0014] バルク重合において、従来通り重合槽内のスラリー濃度を50重量%となるようにして重合を行う場合、濃縮スラリーのスラリー濃度は50重量%より高く75重量%以下、好ましくは50重量%より高く70重量%以下、特に好ましくは60～70重量%の範囲にはいるようにする。スラリー重合においては、従来通り重合槽内のスラリー濃度を35重量%となるようにして重合を行う場合、濃縮スラリーのスラリー濃度は35重量%より高く75重量%以下、好ましくは35重量%より高く60重量%以下、特に好ましくは40～50重量%の範囲にはいるようにする。

[0015] ポリオレフィン粒子を粒径の大きな粒子と小さな粒子に分ける方法としては各種のものが可能であるが、連続運転が極めて容易であり可動部が殆どなく液体の停滞が殆ど無いという点で、特にサイクロンを用いることが好ましい。この他、湿式分級装置や遠心分離機等も好ましく用いられる。

[0016]

[発明の効果] 本発明の連続製造プロセスにおいては、重合系から取り出される濃縮スラリー中の未反応モノマーとポリオレフィン粒子の合計量は、重合槽に新たに仕込まれるモノマーの量に等しくなるので、濃縮スラリー中のスラリー濃度が、仕込みモノマーの転化率に当たることになる。本発明の連続製造プロセスにおいては、濃縮スラリーのスラリーの濃度は重合槽内のスラリー濃度より高いから、従来のバルク重合やスラリー重合と比較してモノマーの転化率を高めることができる。例えば、本発明のプロセスをバルク重合に採用した場合、濃縮スラリーのスラリー濃度は50重量%より高く75重量%まで可能であるから、モノマーの転化率を従来の50重量%に比べ大幅に高めることができる。従って、回収モノマーの量が減少するから、モノマー回収に要するエネルギーは減少し、モノマー回収に要する原材料、ステーム、電力等の原単位も大幅に減少するというメリットもある。又、モノマー回収設備に余力が生まれ回収モノマーの精製度を向

the solvent is reset to polymerization vessel. On one hand, big polyolefin particle of particle diameter is removed outside polymerization system with one part of unreacted monomer and solvent as slurry. Slurry which is removed outside this polymerization system below "concentrated slurry" with we say. As for slurry concentration of concentrated slurry, it is necessary to be larger than that in slurry inside polymerization vessel, but when slurry concentration exceeds 75 weight %, the fluidity of concentrated slurry to become low, because it becomes impossible to remove smoothly outside polymerization system, it is not desirable. Especially desirable slurry concentration is 70 wt% or less.

[0014] When you polymerize in bulk polymerization, until recently sort slurry concentration inside the polymerization vessel to become 50 weight %, try slurry concentration of concentrated slurry to enter into range of 70 wt% or less and particularly preferably 60 to 70 weight % more highly than 50 weight % more highly than 75 wt% or less and preferably 50 weight %. Regarding slurry polymerization, when you polymerize until recently sort slurry concentration inside polymerization vessel to become 35 weight %, try slurry concentration of concentrated slurry to enter into range of 60 wt% or less and particularly preferably 40 to 50 weight % more highly than the 35 weight % more highly than 75 wt% or less and preferably 35 weight %.

[0015] Various ones are possible polyolefin particle as big particle of particle diameter and the method which is divided into small particle, but continuous operation quite is easy and in point that, there is not a movable part almost, almost is not stagnation of liquid it is desirable to use especially cyclone. In addition, also wet classification equipment and centrifugal separator etc are desirably used.

[0016]

[Effects of the Invention] Regarding continuous production process of this invention, as for unreacted monomer in concentrated slurry which is removed from polymerization system and total amount of polyolefin particle, because it becomes equal in quantity of monomer which is inserted in the polymerization vessel anew, slurry concentration in concentrated slurry, means to hit to conversion ratio of the addition monomer. Regarding continuous production process of this invention, because concentration of slurry of the concentrated slurry is higher than slurry concentration inside polymerization vessel, it is possible to raise conversion ratio of monomer, by comparison with conventional bulk polymerization and the slurry polymerization. When process of for example this invention is adopted for bulk polymerization, because the slurry concentration of concentrated slurry to be higher than 50 weight % is possible to the 75 weight %, greatly

上させることができる。更に、粒径の小さい、即ち高活性且つ活性点密度の高い触媒を含むポリオレフィン粒子は、その殆どが重合槽に戻され重合に関与するから、触媒の利用効率も高くできるという特徴がある。そして、これらの粒径の小さな粒子が製品に混入することが少なくなるから、射出成形グレードにおいては耐衝撃性の高い製品が得られ、フィルムグレードにおいてはフィッシュアイの発生を抑えることができる。

【0017】

【実施例】以下、第三世代チーグラー・ナッタ触媒を用いたプロピレンのバルク重合プロセスであって単一の重合槽で重合をおこなうものに本発明の連続製造プロセスを適用した例を挙げて、本発明の連続製造プロセスについて詳しく説明する。

【0018】図1は、本実施例のプロセスの一例であって、ポリオレフィン（ポリプロピレン）粒子を粒径の大きな粒子と粒径の小さな粒子に分けるのにサイクロンを用いた例を示すプロセス図である。図2は、従来のプロピレンのバルク重合プロセスの一例を示すプロセス図である。

【0019】図中、1は重合槽を、2はコンデンサーを、3は固一気分離器を、4は圧縮機を、5はヒーターを、6はポンプを、7はサイクロンを示す。a、b、c、dは各々流量調節弁を示す。8は液化プロピレンを重合槽1に供給するためのラインを、9は重合槽1から蒸発したプロピレン及び水素を含む混合ガスをコンデンサー2に導くためのラインであり、途中には流量調節弁aが設けられている。10はコンデンサー2から液化プロピレンを重合槽1に戻すためのライン、11及び12は、重合槽からポリオレフィン（ポリプロピレン）粒子と液化プロピレンのスラリーを抜き出してサイクロン7に導くためのラインであり、13はポリオレフィン（ポリプロピレン）粒子と液化プロピレンの混合物を重合槽1に戻すラインである。

【0020】以下、図1に示したプロセスの作用について説明する。

it is possible conversion ratio of monomer in comparison with conventional 50 weight % to raise. Therefore, because quantity of recovery monomer decreases,a merit that there is it decreases energy which is required in the monomer recovery, are required in monomer recovery a raw material , a steam , a electric power or other starting unit and the greatly it decreases. Remaining strength is born in also, monomer recovery facility and purity of recovery monomer can improve. Furthermore, particle diameter it is small, namely as for polyolefin particle which includes catalyst where high activity and active site density are high, most to be reset by polymerization vessel, because it participates in polymerization,there is a feature that it can be made also use efficiency of catalyst high. Because and, it decreases, for small particle of these particle diameter to mixto product, product where impact resistance is high regarding injection molding grade is acquired, can hold down occurrence of fisheye regarding the film grade.

[0017]

[Working Example(s)] Below, being a bulk polymerization process of propylene which uses third generation Ziegler-Natta catalyst, listing the example which applies continuous production process of this invention to those which polymerize with single polymerization vessel, you explain in detail concerning continuous production process of the this invention.

[0018] Figure 1, being a one example of process of this working example, although you divide polyolefin (polypropylene) particle into big particle of particle diameter and small particle of particle diameter, is process diagram which shows example which uses the cyclone. Figure 2 is process diagram which shows one example of bulk polymerization process of the conventional propylene.

[0019] As for in the diagram and 1 polymerization vessel, as for 2 condenser, as for 3 solid-gas separator, as for 4 compressor, as for the 5 heater, as for 6 pump, as for 7 the cyclone is shown. a, b, c and d show each flow regulating valve. As for 8 line in order to supply liquified propylene to polymerization vessel 1, the 9 is line in order to lead mixed gas which includes the propylene and hydrogen which evaporate from polymerization vessel 1 to condenser 2, the flow regulating valve a is provided on middle. As for 10 with line in order to reset liquified propylene to the polymerization vessel 1 from condenser 2, 11 and 12, extracting slurry of polyolefin (polypropylene) particle and the liquified propylene from polymerization vessel, is line in order to lead to cyclone 7, the 13 is line which resets blend of polyolefin (polypropylene) particle and the liquified propylene to polymerization vessel 1.

[0020] You explain below, concerning action of process which is shown in Figure 1.

【0021】液化プロピレンはライン8を通って重合槽1に供給される。液化プロピレンの供給量は、重合槽1内部の液面の高さが一定となるように制御される。ライン8の途中から、主触媒、助触媒、及び電子供与体が供給される。主触媒としては例えば塩化チタンを塩化マグネシウムに担持させたものと有機アルミニウム化合物とを反応させたもの、及び予備重合された触媒等が用いられる。又助触媒としては有機アルミニウム化合物を、電子供与体としては各種シラン化合物が用いられる。主触媒、助触媒及び電子供与体は、連続的に供給することができる。重合槽1内部では、ライン8から供給された液化プロピレンが重合し、活性を有する触媒を包含したポリプロピレン粒子として液化プロピレン中に懸濁スラリーとなっている。一方、スラリー中の液化プロピレンの一部は気化し、重合槽1内で発生した重合熱を除去する。そして気化したプロピレンは、プロパン等不純物として含まれていた炭化水素ガスや、分子量調節剤として添加された水素等とともに混合ガスとしてライン9を通してコンデンサー2に導かれる。

【0022】ライン9を通して重合槽1から除去された混合ガスは、コンデンサー2に導かれ、そこで気化プロピレンは液化し、ライン10を通って再び重合槽1に戻される。コンデンサー2に導かれる混合ガスの量は、流量調節弁aの開き度を加減することによって調節される。重合槽1の内圧即ち重合温度は、コンデンサー2に導かれる混合ガスの量を増減することにより調節される。

【0023】重合槽1内で生成したポリプロピレン粒子のスラリーはライン11を通して重合槽1より抜き出され、ライン12を通してサイクロン7に供給される。サイクロン7において、スラリー中のポリプロピレン粒子は粒径の大きな粒子と粒径の小さな粒子に分けられる。粒径の小さな粒子はサイクロン7の上部からスラリーとして回収され、ライン13を通して重合槽1に戻される。一方、粒径の大きな粒子は、濃縮スラリーとなってサイクロン7の底部から流量調節弁bを通して排出され、ライン15を通して固一気分離器3に送られる。濃縮スラリーのスラリー濃度は、流量調節弁b及びcで調節することにより増減できる。濃縮スラリーは、流量調節弁bから排出されると、中に含まれている液化プロピレンが直ちに気化し、低温の気化プロピレンと粒径の大きなポリプロピレン粒子の混合物になる。この混合物はライン16、17、及び19を循環する循環ガスと合流し、固一気分離器3に送られる。尚、濃縮スラリーは断続的に排出することが好ましい。

[0021] Liquified propylene passing by line 8, is supplied to polymerization vessel 1. supplied amount of liquified propylene is controlled, in order for height of the liquid surface of polymerization vessel 1 inside to become fixed. From middle of line 8, main catalyst, cocatalyst, and the electron donor are supplied. Those which bear for example titanium chloride in magnesium chloride as main catalyst and those which react with organo-aluminum compound. It can use catalyst etc which prepolymerization is done. In addition it can use various silane compound with organo-aluminum compound, as electron donor as the cocatalyst. It can supply main catalyst, cocatalyst and electron donor, to continuous. With polymerization vessel 1 inside, liquified propylene which is supplied from line 8 polymerizes, suspension does in liquified propylene as polypropylene particle which includes catalyst which possesses activity and has become slurry. On one hand, portion of liquified propylene in slurry evaporates, removes the heat of polymerization which occurs inside polymerization vessel 1. And propylene which evaporates is led to capacitor 2 through line 9 as impurity hydrocarbon gas which is included and hydrogen which etc such as propane as molecular weight regulator is added and also as mixed gas.

[0022] Mixed gas which is removed from polymerization reactor 1 through line 9 is led by the condenser 2, liquefaction does vaporized propylene there, passes by line 10 and is reset to polymerization reactor 1 again. Quantity of mixed gas which is led to condenser 2 adjusts by allowing open degree of flow regulating valve a. internal pressure namely polymerization temperature of polymerization reactor 1 adjusts by increasing and decreasing quantity of mixed gas which is led to condenser 2.

[0023] Slurry of polypropylene particle which is formed inside polymerization vessel 1 is extracted from polymerization vessel 1 through line 11, is supplied to cyclone 7 through the line 12. In cyclone 7, polypropylene particle in slurry is divided into big particle of the particle diameter and small particle of particle diameter. Small particle of particle diameter recovers as slurry from upper part of the cyclone 7, is reset to polymerization vessel 1 through line 13. On one hand, big particle of particle diameter, becoming concentrated slurry, is discharged to solid-gas separator 3 through line 15 through flow regulating valve b from the bottom part of cyclone 7, is sent. It can increase and decrease slurry concentration of concentrated slurry, by adjusting with the flow regulating valve b and c. As for concentrated slurry, when it is discharged from flow regulating valve b, liquified propylene which is included in evaporates at once, becomes vaporized propylene of the low temperature and blend of big polypropylene particle of particle diameter. line 16, 17, and 19 circulating gas and confluence which circulate it

【0024】固一気分離器3で気化プロピレンとポリプロピレン粒子とが分離され、ポリプロピレン粒子はライン20を通して取り出される。ライン20を通して取り出したポリプロピレン粒子は、必要に応じ脱灰工程、脱アタクチックポリプロピレン工程、乾燥工程、又はペレット化工程に送り、製品として回収することができる。又、ライン20からのポリプロピレン粒子を次の重合槽に供給し、この重合槽に同一または異なるモノマーを追加して、第2段目の重合を行ってよい。第2段目の重合において供給するモノマーとしては、エチレン、プロピレン、1-ブテン、1-ペンテン、4-メチルペンテナ-1、1-ヘキセン、1-オクテンからなる群から選ばれる1種又は2種以上のα-オレフィンが好ましい。

【0025】一方、固一気分離器3で分離された気化プロピレンはライン16、17、及び19を循環する。そして、気化プロピレンの一部はライン18から抜き出され、表示しないモノマー回収工程に送られる。

【0026】以下、実際のポリプロピレンのバルク重合に本発明の連続製造プロセスを適用した例を示す。尚、プロピレンとしては純度95%のものを用いた。不純分は主にプロパンであった。

【0027】得られたポリプロピレン粒子について、以下のようにして物性を測定した。尚、粒径分布、メルトフローレート、及びアイソタクチック部分の割合は脱灰前のポリプロピレン粒子について測定し、フィッシュアイ、Izod衝撃強度、及び射出成形品の外観については、脱灰後のポリプロピレン粒子について測定した。

粒径分布： 目の大きさが74μmの篩、及び目の大きさが840μmの篩でポリプロピレン粒子を分級し、粒径74μm未満のポリプロピレン粒子及び粒径840μmを超える粒径のポリプロピレン粒子の割合を求めた。

メルトフローレート(MF)：ASTM D1238に準拠して測定した。

アイソタクチック部分の割合(HI)：得られたポリプロピレン粒子を、ホットプレスにより0.1mm厚さのフィルムとし、そのフィルムを1cm角に裁断し、この裁断フィルムを、ソックスレー抽出器を用いて沸騰ノルマルヘプタンで6時間抽出し、不溶解分の割合を測定した。

does this blend, is sent to solid-gas separator 3. Furthermore as for concentrated slurry it is desirable to discharge in the discontinuous.

[0024] Vaporized propylene and polypropylene particle are separated with solid-gas separator 3, polypropylene particle is removed through line 20. As for polypropylene particle which is removed through line 20, according to need the demetallization step. atactic polypropylene removal step. You send to drying process or pelletizing step, you can recover as product. It supplies polypropylene particle from also, line 20 to following polymerization vessel, to this polymerization vessel adds identical or different monomer, is possible to polymerize second step. -olefin of one, two or more kinds which is chosen from group which consists of ethylene, propylene, 1-butene, 1-pentene, 4-methylpentene-1, 1-hexene and 1-octene as monomer which is supplied at time of polymerizing second step, is desirable.

[0025] Vaporized propylene which on one hand, is separated with solid-gas separator 3 circulates the line 16, 17, and 19. And, portion of vaporized propylene is extracted from line 18, is sent to the monomer recovery step which is not indicated.

[0026] Below, example which applies continuous production process of this invention to bulk polymerization of actual polypropylene is shown. Furthermore those of purity 95% were used as propylene. impure fraction was propane mainly.

[0027] Property was measured concerning polypropylene particle which it acquires, like below. Furthermore it measured concerning polypropylene particle after demetallization concerning external appearance of fisheye, Izod impact strength, and injection molded article, it measured ratio of particle diameter distribution, melt flow rate, and isotactic portion concerning polypropylene particle before demetallization.

Particle diameter distribution : Size of eye sieve of 74 m, size of eye with sieve of 840 m, classification did polypropylene particle, sought polypropylene particle under particle diameter 74 m and ratio of polypropylene particle of the particle diameter which exceeds particle diameter 840 m.

Conforming to melt flow rate (MF): ASTM D1238, it measured.

Ratio of isotactic portion (HI): polypropylene particle which is acquired, to designate as film of the 0.1 mm thickness with hot press, to cut off film in 1 cm square, 6 hours it extracted with boiling normal heptane this cut film, making use of Soxhlet extractor, measured ratio of insoluble fraction.

フィッシュアイ： Tダイを用いて厚み25 μmのフィルムを得、このフィルムについてヒューテック製フィッシュアイカウンターでフィッシュアイの個数を測定し、450 cm²当たりの個数を表した。

Izod衝撃強度：ASTM D256に準拠して測定した。

射出成形品の外観：Izod衝撃強度の測定に用いたテストピースについて目視で外観を評価した。

【0028】[実施例1] 図1のプロセスでプロピレンのバルク重合を行った例を示す。この実施例においては重合槽1には200リットルの攪拌機付重合槽を用いた。

【0029】先ず、主触媒の調製方法について述べる。30リットルの攪拌機を備えたジャケット付予備重合槽に、ノルマルヘプタン15リットルを仕込み、これを10°Cに保持しつつ、トリエチルアルミニウム(TEA)の15重量%ノルマルヘプタン溶液0.7リットルを仕込んだ。更に、t-ブチルエチルジメトキシラン(TBEDMS)の0.1mol/lリットルノルマルヘプタン溶液0.7リットルを仕込み、東邦チタニウム株式会社製THC-32A触媒を500g充填した。予備重合槽内は窒素ガスで0.5kg/cm²Gに加圧した。ここで、THC-32A触媒は変性された塩化マグネシウム上に塩化チタンを担持させたものである。次いで、プロピレンガス500gを当該予備重合槽に圧入した。圧入時は圧力2.0kg/cm²Gに保持したが、40分経過後圧力は0.5kg/cm²Gとなり予備重合は完了した。得られた主触媒はスラリー状であり、固体分濃度は61g/lリットルであった。当該スラリーを定量的に重合槽に供給することにより、以下の重合反応に供した。

【0030】次に、重合について述べる。重合は、200リットルの攪拌機を備えたジャケット付重合槽を行い、110リットルの液量で重合を行った。助触媒としてはTEAを、電子供与体としてはTBE DMSを用いた。モノマーである液化プロピレンは、重合槽1内部の液面の高さが一定になるように、ライン8から供給した。プロピレンのフィード量は36,500g/hrであった。主触媒は、THC-32A触媒換算で0.5g/hr、TEA及びTBE DMSは、各々純品換算で6.4g/hr及び1.5g/hrの割合で重合槽1に供給した。分子量調節用の水素ガスは、重合して得られたポリプロピレン粒子のメルトフローレートが80となるように、重合槽1に供給した。このときの供給量は233ノルマルリットル/hrであった。

Fisheye: You obtained film of thickness 25 m making use of T-die, you measured number of fisheye with Hutech Origine, K.K. (DN 70-542-7383) make fisheye counter concerning this film, displayed with number of per 450 cm².

Izod impact strength: Conforming to ASTM D256, it measured.

External appearance of injection molded article: external appearance was appraised with visual concerning test piece which is used for measurement of Izod impact strength.

[0028] [Working Example 1] Example which did bulk polymerization of propylene with process of the Figure 1 is shown. mixer-equipped polymerization vessel of 200 liter was used to polymerization vessel 1 regarding this Working Example.

[0029] First, you express concerning preparation method of main catalyst. While inserting normal heptane 15 liter in jacketed prepolymerization tank which has mixer of the 30 liter, keeping this in 10 °C, you inserted 15 weight % normal heptane solution 0.7 liter of triethyl aluminum(TEA). Furthermore, you inserted 0.1 mol/liter normal heptane solution 0.7 liter of t-butyl ethyl dimethoxy silane(TBEDMS), Toho Titanium Co. Ltd. (DN 69-057-0528) make THC-32A catalyst the 500g were filled. With nitrogen gas it pressurized inside prepolymerization tank in 0.5 kg/cm²G. Here, THC-32A catalyst is something which bears titanium chloride on magnesium chloride which the modified is done. Next, propylene gas 500g pressure insertion was done in this said prepolymerization tank. You kept time of pressure insertion in pressure 2.0 kg/cm²G, but after 40 min elapsing the pressure became 0.5 kg/cm²G and completed prepolymerization. main catalyst which is acquired was slurry, solid component concentration was the 61 g/liter. It offered to polymerization reaction below this said slurry by supplying to polymerization vessel in the quantitative.

[0030] Next, you express concerning polymerization. polymerization polymerized with liquid volume of 110 liter making use of jacketed polymerization vessel which has mixer of 200 liter. TBE DMS was used with TEA, as electron donor as cocatalyst. In order for height of liquid surface of polymerization vessel 1 inside to become fixed, its supplied liquified propylene which is a monomer, from line 8. feed amount of propylene was 36,500 g/hr. main catalyst, with THC-32A catalyst conversion with each pure product conversion supplied 0.5 g/hr, the TEA and TBE DMS, to polymerization vessel 1 at ratio of 6.4 g/hr and the 1.5 g/hr. polymerizing, in order for melt flow rate of polypropylene particle which it acquires to become 80, it supplied hydrogen gas for molecular weight adjustment, to the polymerization vessel

[0031] 重合は 78 °C で行った。

[0032] 生成したスラリーを、重合槽 1 の底部に設けられたライン 11 を通し連続的に抜き出し、ポンプ 6 によりサイクロン 7 に送り込み、粒径の大きな粒子のスラリーと粒径の小さな粒子のスラリーに分けた。粒径の大きな粒子のスラリーはサイクロン 7 の底部から濃縮スラリーとして抜き出し、粒径の小さな粒子のスラリーはサイクロン 7 の上部から抜き出し、ライン 13 を通して重合槽 1 内に戻した。濃縮スラリーは、ライン 14 を通し流量調節弁 b を断続的に開閉してライン 15 に送り込んだ。濃縮スラリーのスラリー濃度は、流量調節弁 c の開き度を調整することにより 55 重量% に調整した。当該濃縮スラリー中の液化プロピレンは流量調整弁 b の出口で気化し、濃縮スラリーはポリプロピレン粒子と気化したプロピレンとの混合物となった。流量調整弁 b を出た混合物を、固一気分離器（バッグフィルター）3 に送り込み、ポリプロピレン粒子と、気化プロピレンとに分離し、ポリプロピレン粒子をポリプロピレン粉末として回収した。1 時間あたり回収されたポリプロピレン粉末の量は 20. 1 kg であった。回収されたポリプロピレン粉末は、脱灰用の混合液中で、触媒抽出及び洗浄を行い、脱灰した。脱灰は以下のようにして行った。先ず、スラリー濃度 20 重量% となるように混合液中にポリプロピレン粒子を懸濁させて 85 °C、30 分の条件でポリプロピレン粒子中の触媒を抽出・除去し、次いで、このポリプロピレン粒子に混合液を 85 °C で吹き付けて洗浄した。触媒抽出と洗浄は 2 回繰り返した。脱灰後のポリプロピレン粒子は、60 °C、10 torr の条件で 12 時間乾燥した。一方、固一気分離器 3 で分離した気化プロピレンは、圧縮機 4 及びヒーター 5 を通し、ライン 16、17 及び 19 からなる循環ラインを循環させるとともに、その一部をライン 18 から抜き出し、循環量が一定になるようにした。

[0033] 運転は安定して行えた。又、得られたポリプロピレンは、メルトフローレート (MFR) が 80、アイソタクチック構造割合 (H1) が 98. 7 % であった。粒径分布は、ポリプロピレン粒子全体 100 重量% の内、粒径 74 μm 未満のものが 1. 0 重量%、粒径 840 μm よりも大きなものが 25. 5 重量% であった。又、アイソッド衝撃強度は 5. 5 kgf · cm/cm² と優れる一方、フィッシュアイの個数は 6 個 / 450 cm² に過ぎなかった。得られた射出成形品の表面状態は極めて平滑であった。

1. supplied amount of this time was 233 normal liter/h.

[0031] You polymerized with 78 °C .

[0032] Through line 11 which can provide slurry which it forms, in the bottom of polymerization vessel 1 sending to cyclone 7 in continuous due to the extract and pump 6 , you divided into slurry of big particle of the particle diameter and slurry of small particle of particle diameter. As for slurry of small particle of extract and particle diameter you're set into polymerization vessel 1 through extract and line 13 from upper part of cyclone 7 as for slurry of big particle of particle diameter as the concentrated slurry from bottom of cyclone 7. As for concentrated slurry, opening and closing flow regulating valve b in discontinuous through the line 14, you sent to line 15. You adjusted slurry concentration of concentrated slurry, 55 weight % by adjusting open degree of flow regulating valve c. liquefied propylene in this said concentrated slurry evaporated with outlet of flow adjustment valve b, the concentrated slurry polypropylene particle and became blend of propylene which evaporates. Sending blend which comes out of flow adjustment valve b, to solid-gas separator (bag filter)3 , it separated with into polypropylene particle and vaporized propylene, it recovered with the polypropylene particle as polypropylene powder. per hour quantity of polypropylene powder which recovers was 20.1 kg. polypropylene powder which recovers extracted, washed, did, in the mixed solution for demetallization, catalyst and demetallization. demetallization did like below. First, in order to become slurry concentration 20 weight %, suspension doing polypropylene particle in the mixed solution, extraction * it removed catalyst in polypropylene particle with the condition of 85 °C and 30 min, next, in this polypropylene particle blew the mixed solution with 85 °C and washed. 2 time it repeated catalyst extraction and washing. 1 2 hours it dried polypropylene particle after demetallization, with condition of the 60 °C and 10 torr. vaporized propylene which on one hand, is separated with solid-gas separator 3, circulation line which consists of line 16, 17 and 19 through compressor 4 and the heater 5, as it circulates, from line 18 extract and recycle quantity tried part of that that become fixed.

[0033] Stabilizing, it could do driving. also, as for polypropylene which is acquired, melt flow rate (MFR) being the 80, proportion of isotactic structure (H1) was 98. 7 %. As for particle diameter distribution, things such as among polypropylene particle entirely 100 weight % and under particle diameter 74 mbigger ones than 1. 0 weight % and particle diameter 840 m was 25. 5 weight %. As for also, Izod impact strength although 5. 5 kgf-cm/cm it is superior number of the fisheye was no more than a 6 /450 cm². surface state of injection molded article which is acquired was quite smooth.

【0034】[実施例2] 濃縮スラリーのスラリー濃度を60重量%に調整した以外は、実施例1と同様にして実施した。このときのプロピレンの供給量は33,700 g/hr、水素の供給量は203ノルマルリットル/hrであった。そして1時間あたり回収されたポリプロピレン粉末の量は20.2 kgであった。運転は安定して行えた。又、得られたポリプロピレンは、メルトフローレート(MFR)が80、アイソタクチック構造割合(HI)が98.7%であり、粒径分布は、ポリプロピレン粒子全体100重量%の内、粒径74 μm未満のものが0.7重量%、粒径840 μmよりも大きなものが26.0重量%であった。アイソッド衝撃強度は6.0 kgf·cm/cmと優れる一方、フィッシュアイの個数は4個/450 cm²に過ぎなかった。得られた射出成形品の表面状態は極めて平滑であった。

【0035】[実施例3] 濃縮スラリーのスラリー濃度を65重量%に調整した以外は、実施例1と同様にして実施した。このときのプロピレンの供給量は31,500 g/hr、水素の供給量は178ノルマルリットル/hrであった。そして1時間あたり回収されたポリプロピレン粉末の量は20.5 kgであった。運転は安定して行えた。又、得られたポリプロピレンは、メルトフローレート(MFR)が80、アイソタクチック構造割合(HI)が98.7%であり、粒径分布は、ポリプロピレン粒子全体100重量%の内、粒径74 μm未満のものが0.5重量%、粒径840 μmよりも大きなものが26.5重量%であった。アイソッド衝撃強度は6.5 kgf·cm/cmと優れる一方、フィッシュアイの個数は3個/450 cm²に過ぎなかった。得られた射出成形品の表面状態は極めて平滑であった。

【0036】[実施例4] 濃縮スラリーのスラリー濃度を70重量%に調整した以外は、実施例1と同様にして実施した。このときのプロピレンの供給量は30,000 g/hr、水素の供給量は158ノルマルリットル/hrであった。そして1時間あたり回収されたポリプロピレン粉末の量は21.0 kgであった。運転は安定して行えた。又、得られたポリプロピレンは、メルトフローレート(MFR)が80、アイソタクチック構造割合(HI)が98.8%であり、粒径分布は、ポリプロピレン粒子全体100重量%の内、粒径74 μm未満のものが0.5重量%、粒径840 μmよりも大きなものが26.0重量%であった。アイソッド衝撃強度は6.5 kgf·cm/cmと優れる一方、フィッシュアイの個数は3個/450 cm²に過ぎなかった。得られた射出成形品の表面状態は極めて平滑であった。

[0034] [Working Example 2] Other than adjusting slurry concentration of concentrated slurry 60 weight %, it executed in the same way as Working Example 1. As for supplied amount of propylene of this time with 33,700 g/hr, as for the supplied amount of hydrogen it was a 203 normal liter/h. And per hour quantity of polypropylene powder which recovers was 20.2 kg. Stabilizing, it could do driving. also, as for polypropylene which is acquired, melt flow rate (MFR) 80 and the proportion of isotactic structure (HI) was 98.7%, as for particle diameter distribution, things such as among the polypropylene particle entirely 100 weight % and under particle diameter 74 m being 0.7 weight %, bigger ones than particle diameter 840 m were 26.0 weight %. As for Izod impact strength although 6.0 kgf-cm/cm it is superior number of the fisheye was no more than a 4/450 cm². surface state of injection molded article which is acquired was quite smooth.

[0035] [Working Example 3] Other than adjusting slurry concentration of concentrated slurry 65 weight %, it executed in the same way as Working Example 1. As for supplied amount of propylene of this time as for supplied amount of the 31,500 g/hr and hydrogen it was a 178 normal liter/h. And per hour quantity of polypropylene powder which recovers was 20.5 kg. Stabilizing, it could do driving. also, as for polypropylene which is acquired, melt flow rate (MFR) being the 80, proportion of isotactic structure (HI) was 98.7%, as for particle diameter distribution, things such as among the polypropylene particle entirely 100 weight % and under particle diameter 74 m being 0.5 weight %, bigger ones than the particle diameter 840 m were 26.5 weight %. As for Izod impact strength although 6.5 kgf-cm/cm it is superior number of the fisheye was no more than a 3/450 cm². surface state of injection molded article which is acquired was quite smooth.

[0036] [Working Example 4] Other than adjusting slurry concentration of concentrated slurry 70 weight %, it executed in the same way as Working Example 1. As for supplied amount of propylene of this time as for supplied amount of the 30,000 g/hr and hydrogen it was a 158 normal liter/h. And per hour quantity of polypropylene powder which recovers was 21.0 kg. Stabilizing, it could do driving. also, as for polypropylene which is acquired, melt flow rate (MFR) 80 and the proportion of isotactic structure (HI) was 98.8%, as for particle diameter distribution, things such as among the polypropylene particle entirely 100 weight % and under particle diameter 74 m being 0.5 weight %, bigger ones than particle diameter 840 m were 26.0 weight %. As for Izod impact strength although 6.5 kgf-cm/cm it is superior number of the fisheye was no more than a 3/450 cm². surface state of injection molded article which is acquired was quite smooth.

【0037】[実施例5] 濃縮スラリーのスラリー濃度を75重量%に調整した以外は、実施例1と同様にして実施した。このときのプロピレンの供給量は25,300 g/hr、水素の供給量は131ノルマルリットル/hrであった。そして1時間あたり回収されたポリプロピレン粉末の量は19.0 kgであった。運転は安定して行えたが、濃縮スラリーの抜き出しに若干の変動が見られた。得られたポリプロピレンは、メルトフローレート(MFR)が80、アイソタクチック構造割合(HI)が98.8%であり、粒径分布は、ポリプロピレン粒子全体100重量%の内、粒径74 μm未満のものが0.5重量%、粒径840 μmよりも大きなものが26.0重量%であった。アイゾッド衝撃強度は6.5 kgf·cm/cmと優れる一方、フィッシュアイの個数は5個/450 cm²に過ぎなかった。得られた射出成形品の表面状態は平滑であった。

【0038】[比較例1] 図2に示す従来のプロセスでプロピレンのバルク重合を行い、重合槽1へのプロピレンのフィード量が40,000 g/hrとなつた以外は、実施例1と同様に実施した。1時間当たりのポリプロピレン粉末の回収量は20.0 kg/hrであった。得られたポリプロピレンは、メルトフローレート(MFR)が80、アイソタクチック構造割合(HI)が98.7%であり、粒径分布は、ポリプロピレン粒子全体100重量%の内、粒径74 μm未満のものが3.0重量%、粒径840 μmよりも大きなものが25.0重量%であった。アイゾッド衝撃強度は4.5 kgf·cm/cmと劣る一方、フィッシュアイの個数は15個/450 cm²もあった。得られた射出成形品の表面状態は良好であった。

【0039】

[0037] [Working Example 5] Other than adjusting slurry concentration of concentrated slurry 75 weight %, it executed in the same way as Working Example 1. As for supplied amount of propylene of this time as for supplied amount of the 25,300 g/hr and hydrogen it was a 131 normal liter/h. And per hour quantity of polypropylene powder which recovers was 19.0 kg. As for driving stabilizing, it could do, but, you could see somewhat fluctuation to extract of concentrated slurry. as for polypropylene which is acquired, melt flow rate (MFR) 80 and the proportion of isotactic structure (HI) was 98.8%, as for particle diameter distribution, things such as among the polypropylene particle entirely 100 weight % and under particle diameter 74 m bigger ones than 0.5 weight % and particle diameter 840 m wasthe 26.0 weight %. As for Izod impact strength although 6.5 kgf-cm/cm it is superior number of the fisheye 5 was no more than a /450 cm². surface state of injection molded article which is acquired was smooth.

[0038] [Comparative Example 1] It did bulk polymerization of propylene with conventional process which is shown in the Figure 2, other than feed amount of propylene to polymerization vessel 1 had become the 40,000 g/hr. it executed in same way as Working Example 1. recovered amount of polypropylene powder of per hour was 20.0 kg/h. as for polypropylene which is acquired, melt flow rate (MFR) 80 and the proportion of isotactic structure (HI) was 98.7%, as for particle diameter distribution, things such as among the polypropylene particle entirely 100 weight % and under particle diameter 74 m bigger ones than 3.0 weight % and particle diameter 840 m wasthe 25.0 weight %. As for Izod impact strength although 4.5 kgf-cm/cm it is inferior 15 the/450 cm² there was a number of fisheye. surface state of injection molded article which is acquired was good.

[0039]

【表1】

[Table 1]

| | 実施例 | 比較例 | | | | |
|-----------------|-------------------|-------|-------|-------|--------|------|
| | | 1 | 2 | 3 | 4 | 5 |
| 重合温度 (°C) | 78 | 同左 | 同左 | 同左 | 同左 | 同左 |
| 液量 (リットル) | 110 | 同左 | 同左 | 同左 | 同左 | 同左 |
| 主触媒供給量 (g/hr) | 0.5 | 同左 | 同左 | 同左 | 同左 | 同左 |
| TEA供給量 (g/hr) | 6.4 | 同左 | 同左 | 同左 | 同左 | 同左 |
| TBEDMS (g/hr) | 1.5 | 同左 | 同左 | 同左 | 同左 | 同左 |
| 水素 (ml/hr) | 233 | 203 | 178 | 158 | 131 | 269 |
| 重合槽内MFR濃度 (wt%) | 50 | 50 | 50 | 50 | 50 | 50 |
| 液相MFR-濃度 (wt%) | 55 | 60 | 65 | 70 | 75 | 50 |
| 結果 | プロピレン供給量 (kg/hr) | 36.5 | 33.7 | 31.5 | 30.0 | 25.3 |
| | リバーアクション量 (kg/hr) | 20.1 | 20.2 | 20.5 | 21.0 | 19.0 |
| 運転安定性 | 良好 | 良好 | 良好 | 良好 | 若干の変動有 | 良好 |
| MP(g/10分) | 8.0 | 8.0 | 8.0 | 8.0 | 8.0 | 8.0 |
| H.I (%) | 98.7 | 98.7 | 98.7 | 98.8 | 98.8 | 98.7 |
| 粒径分布 < 74 μm | 1.0 | 0.7 | 0.5 | 0.5 | 0.5 | 3.0 |
| > 840 μm | 25.5 | 26.0 | 26.5 | 26.0 | 26.0 | 25.0 |
| ノックダウン個数 | 6 | 4 | 3 | 3 | 5 | 15 |
| Izod衝撃強度 | 5.5 | 6.0 | 6.5 | 6.5 | 6.5 | 4.5 |
| 射出成形品外観 | 極めて良好 | 極めて良好 | 極めて良好 | 極めて良好 | 極めて良好 | 良好 |

[0040]

【図面の簡単な説明】

【図1】 本発明の連続製造プロセスをポリプロピレンのバルク重合に適用した例を示すプロセス図

【図2】 従来のポリプロピレンのバルク重合のプロセスを示すプロセス図

【符号の説明】

[0040]

[Brief Explanation of the Drawing(s)]

[Figure 1] Process diagram which shows example which applies continuous production process of this invention to bulk polymerization of polypropylene.

[Figure 2] Process diagram which shows process of bulk polymerization of conventional polypropylene.

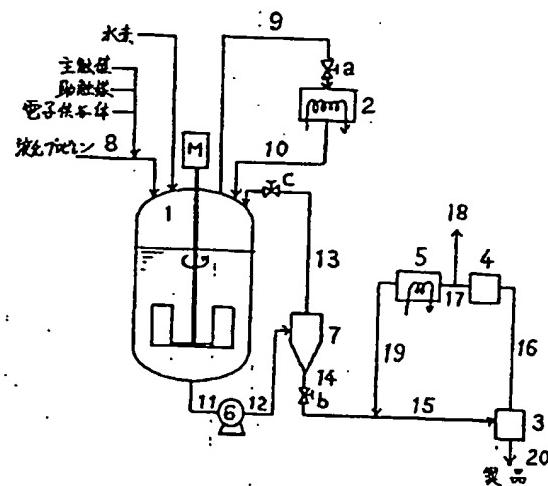
[Explanation of Reference Signs in Drawings]

- 1 聚合槽
 2 コンデンサー
 3 固一気分離器
 4 圧縮機
 5 ヒーター
 6 ポンプ
 7 サイクロン
 8 液化プロピレンを重合槽 1 に供給するためのライン
 9 重合槽 1 からの混合ガスをコンデンサー 2 に導くためのライン
 10 コンデンサー 2 からの液化プロピレンを重合槽 1 に戻すためのライン
 11 及び 12 ポリオレフィン (ポリプロピレン) 粒子と液化プロピレンのスラリーを重合槽から抜き出してサイクロン 7 に導くためのライン
 13 ポリオレフィン (ポリプロピレン) 粒子と液化プロピレンのスラリーを重合槽 1 に戻すラインである。

- 1 * * * polymerization vessel
 2 * * * capacitor
 3 * * * solid-gas separator
 4 * * * compressor
 5 * * * heater
 6 * * * pump
 7 * * * cyclone
 8 * * *. line in order to supply liquified propylene to polymerization vessel 1.
 9 * * *. line in order to lead mixed gas from polymerization vessel 1 to capacitor 2.
 10 * * *. line in order to reset liquified propylene from capacitor 2 to polymerization vessel 1.
 11 and 12 * * *. Extracting slurry of polyolefin (polypropylene) particle and liquified propylene from polymerization vessel, theline in order to lead to cyclone 7.
 13 * * *. It is a line which resets slurry of polyolefin (polypropylene) particle and liquified propylene to thepolymerization vessel 1.

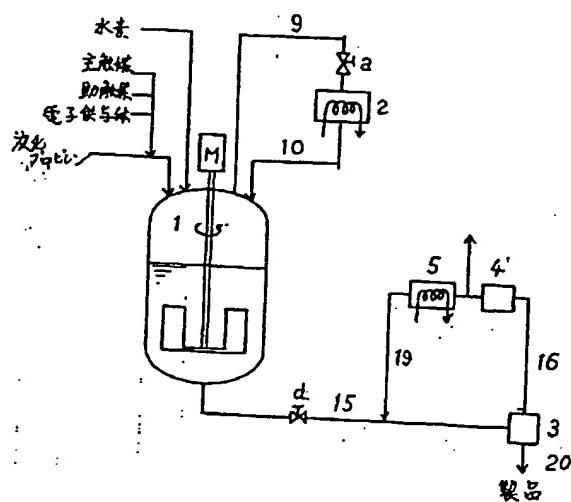
【図 1】

[Figure 1]



[図2]

[Figure 2]



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Title of Invention: Continuous polyolefin production process
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Abstract

Make-up of Invention: In a process in which polypropylene is manufactured by slurry or bulk polymerization of propylene, etc., the slurry in the polymerization vessel is continuously extracted and the polypropylene particles in the slurry are continuously classified by means of a cyclone, etc.; only the slurry containing the small-diameter polypropylene particles is returned to the polymerization vessel, and the slurry containing the large-diameter polypropylene particles is recovered as the product.

Effects of Invention: The utilization efficiency of the polymerization catalyst is improved and the yield of polypropylene with respect to the quantity of propylene charged is raised.

Specifications

1. Title of Invention:

Continuous polyolefin production process

2. Claims:

(1) A continuous polyolefin production process, characterized in that, in a process in which polypropylene is manufactured by slurry or bulk polymerization of olefin monomers using 1 or more polymerization vessels and a stereoregular catalyst; (a) the slurry in the polymerization vessel is continuously extracted, (b) the polypropylene particles in the slurry are continuously classified by means of a cyclone, etc., obtaining a slurry which has a slurry concentration higher than that of the slurry in the polymerization vessel and in which the polyolefin particles are constituted primarily of larger-diameter ones; and (c) this slurry is removed from the polymerization system and the remainder of the slurry which was extracted from the polymerization vessel is returned to this vessel.

3. Detailed Explanation of Invention:

Industrial Field of Application

This invention concerns an improved continuous polyolefin production process in which olefin monomers are continuously polymerized by means of a stereoregular catalyst, such as a Ziegler-Natta catalyst, in a polymerization vessel connected to 1 polymerization vessel or a series of 2 or more vessels.

Prior Art

Polyolefins, such as high-density polyethylene, linear low-density polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-propylene rubber, ethylene-propylene-diene copolymer, etc., are often manufactured continuously by a process of slurry or bulk, etc., polymerization, in a single polymerization vessel or a series of 2 or more vessels, using a stereoregular catalyst such as a Ziegler-Natta catalyst. In these processes, the polyolefins are recovered as particles which include the catalyst inside them.

In the slurry and bulk polymerization processes, in order to increase the conversion rate with respect to the quantity of monomer fed, the method of raising the slurry concentration in the polymerization vessel has been investigated. However, it was found previously that if the slurry concentration in the vessel becomes too high during the slurry or bulk polymerization, the problem arises that stirring becomes difficult and uniform polymerization becomes difficult. For example, in the polymerization of propylene by slurry polymerization, a slurry concentration of 35 wt % is said to be the limit for performing stable operation of the process. In bulk polymerization, on the other hand, the limit for stable operation is said to be about 50 wt %.

Up to now, in bulk polymerization, the slurry in the polymerization vessel was continuously removed from a removal line provided to the polymerization vessel. This is because the internal pressure of the polymerization vessel is high, 20-60 kg/cm² G, whereas the pressure in the removal line is lower, 1-10 kg/cm² G. By continuously extracting the slurry in this manner, the internal pressure of the polymerization vessel could be maintained and the quantity of slurry extracted could be controlled by controlling the timing of the valve openings and closings.

Problems That the Invention Is to Solve

Up to now, the slurry in the polymerization vessel was only continuously extracted as is, in this manner; therefore, the slurry concentration in the polymerization vessel became the conversion rate to polyolefin particles, per unit quantity of monomer fed into the process, and this conversion rate could not exceed the limits mentioned above. Furthermore, the slurry which was extracted contained a large quantity of small-diameter polyolefin particles. These small-diameter particles had not yet progressed very far in the polymerization process; the active site density of the catalyst in the particles was high, and the activity was still quite high. Therefore, the problem arose that the still highly active catalyst, in the form of being contained in the polyolefin particles, was given a short path and thus had a low utilization efficiency, which reduced productivity. In addition, since the polyolefin particles with small diameters

and high active site densities, i.e., short residence times, were mixed in with the product, fish eyes tended to be easily produced in film-grade polymers, while in injection-molding-grade polymers, molded articles with high impact resistances could not be obtained. There was also the problem that surface roughening was easily produced in molded articles.

Furthermore, since the slurry in the polymerization vessel was extracted as is from the removal line, as mentioned above, a large quantity of monomer was also extracted together with the polyolefin particles. For this reason, a large quantity of monomer had to be recovered, and as a result the problems arose that the monomer recovery apparatus became large and the amount of energy required for the monomer recovery became large. This invention has the purpose of improving the productivity and catalyst utilization efficiency in processes such as conventional slurry or bulk polymerization.

Means of Solving the Problems

This invention is characterized by the fact that, in a process in which polypropylene is manufactured by slurry or bulk polymerization of olefin monomers using 1 or more polymerization vessels and a stereoregular catalyst; (a) the slurry in the polymerization vessel is continuously extracted, (b) the polypropylene particles in the slurry are continuously classified by means of a cyclone, etc., obtaining a slurry which has a slurry concentration higher than that of the slurry in the polymerization vessel and in which the polyolefin particles are constituted primarily of larger-diameter ones; and (c) this slurry is removed from the polymerization system and the remainder of the slurry which was extracted from the polymerization vessel is returned to this vessel.

The continuous production process of this invention can be applied to the production of various kinds of polyolefins. Specifically, it can be applied to the production of high-density polyethylene, linear low-density polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-propylene rubber, ethylene-propylene-diene copolymer, etc.

Examples of the olefin monomers which can be used in the process are a-olefins with carbon numbers of 2-8. Specifically, one can use 1 or more kinds of a-olefins selected from ethylene, propylene, 1-butene, 1-pentene, 4-methylpentene-1, 1-hexene, and 1-octene.

The catalysts which can be used are stereoregular catalysts, specifically, Ziegler-Natta catalysts for manufacturing polypropylene, including $TiCl_3-AlR_3$ (where R is an alkyl group) catalysts; $TiCl_4-AlR_2X$ (where X is a halogen) catalysts; ones which contain these catalysts supported on magnesium chloride or magnesium hydroxide; Ziegler-Natta catalysts for manufacturing polyethylenes made by reacting $TiCl_3-AlR_3$ or $TiCl_4-AlR_2X$ catalysts

with magnesium alkoxides; first-generation Ziegler-Natta catalysts, such as TiCl₃-AlR₂X catalysts; second-generation Ziegler-Natta catalysts, such as so-called Solvay catalysts; third-generation Ziegler-Natta catalysts prepared by combining supported solid catalysts consisting of titanium halides supported on magnesium halides and containing diesters of phthalic acid, etc., as internal donors, organoaluminum compounds, and external donors, such as silane compounds; etc. Other desirable catalysts are ones for manufacturing ethylene-propylene rubber which contain as their principal components V compounds, such as VOC₁₃ and VC₁₄, etc., and organoaluminum compounds, such as ethyl aluminum sesquichloride, etc.

Examples of the polymerization process in which the continuous production process of this invention can be applied are methods of continuous polymerization using individual polymerization vessels or 2 or more polymerization vessels connected in series.

Specifically, it is desirable for slurry, bulk, etc., polymerization. The term "slurry polymerization" here refers to processes in which the polymerization is performed in solvents in which the olefin monomers do not dissolve but the polyolefins produced do dissolve. On the other hand, the term "bulk polymerization" refers to processes in which the polymerization is performed in the olefin monomers.

In the continuous production process of this invention, the polyolefin particles are extracted from the polymerization vessel as a slurry, together with the unreacted monomers and the solvent, and the polyolefin particles in the slurry are separated into large and small particles. The small-diameter polyolefin particles are returned to the polymerization vessel together with most of the unreacted monomers and the solvent. On the other hand, the large-diameter particles are removed from the polymerization vessel as a slurry, together with some of the unreacted monomers and solvent. The slurry removed from the polymerization vessel will be referred to below as the "concentrated slurry." The slurry concentration of the concentrated slurry must be larger than that of the slurry in the polymerization vessel, but if it exceeds 75 wt %, the fluidity of the concentrated slurry will be reduced and it will no longer be able to be removed smoothly from the system; therefore, this is not desirable. Especially desirable slurry concentrations are 70 wt % or less.

In bulk polymerization, when the polymerization is performed in such a way that the slurry concentration in the polymerization vessel becomes 50 wt %, as was formerly done, the slurry concentration of the concentrated slurry is greater than 50 wt % and less than 75 wt %, preferably from 50 to 70 wt %, and especially preferably 60-70 wt %. In slurry polymerization, when the polymerization is performed in such a way that the slurry concentration in the polymerization vessel becomes 35 wt %, as was

formerly done, the slurry concentration of the concentrated slurry is greater than 35 wt % and less than 75 wt %, preferably from 35 to 60 wt %, and especially preferably 40-50 wt %.

Various methods can be used for separating the polyolefin particles into large- and small-diameter particles, but the use of a cyclone is especially desirable from the points of view that it makes continuous operation extremely easy and there is almost no stagnation of the liquid. Other desirable methods are wet classification devices, centrifugal separators, etc.

Operation of Invention

In the continuous production process of this invention, the total quantity of the unreacted monomer and polyolefin particles in the concentrated slurry removed from the polymerization system becomes equal to the quantity of the monomer newly charged into the polymerization vessel; therefore, the slurry concentration in the concentrated slurry is aligned with the conversion rate of the charged monomer. In the continuous production process of this invention, since the slurry concentration of the concentrated slurry is higher than the slurry concentration in the polymerization vessel, the conversion rate of the monomer can be made higher than in the conventional bulk and slurry polymerization methods. For example, when the process of this invention is employed in bulk polymerization, the slurry concentration of the concentrated slurry can be higher than 50 wt % and up to 75 wt %; therefore, the conversion rate of the monomer can be greatly raised, compared with the 50 wt % obtained previously. Consequently, there is the advantage that, since the quantity of the recovered monomer is decreased, the energy required for the monomer recovery is decreased and the units of the raw materials, steam, electrical power, etc., required in the monomer recovery are also greatly decreased. Moreover, excess power is produced in the monomer recovery apparatus and the degree of purity of the recovered monomer can be increased. In addition, the polyolefin particles with small diameters, i.e., those which contain catalyst with high active site densities and high activities, are returned almost entirely to the polymerization vessel, so that the advantage of raising the efficiency of utilization of the catalyst is obtained. Furthermore, since these small-diameter particles are not mixed with the product, products with high impact resistance are obtained in the injection-molding grade, and the production of fish eyes is kept down in the film grade.

Working Examples

Examples of applying the continuous manufacturing process of this invention to polymerization in a single polymerization vessel using a bulk polymerization process of propylene, using a third-generation Ziegler-Natta catalyst will be given below, in order to explain the continuous manufacturing process of this

invention in more detail.

Fig. 1 shows an example of the process of the working examples; it is a process drawing which shows an example of the use of a cyclone to separating large- and small-diameter polyolefin (polypropylene) particles. Fig. 2 is a process drawing which shows an example of the conventional bulk propylene polymerization process.

In these diagrams, 1 is a polymerization vessel, 2 is a condenser, 3 is a solid-gas separator, 4 is a compressor, 5 is a heater, 6 is a pump, and 7 is a cyclone. a, b, c, and d are flow regulating valves. 8 is a line for feeding liquefied propylene to the polymerization vessel 1, 9 is a line for carrying a mixed gas containing vaporized propylene and hydrogen from the polymerization vessel 1 to the condenser 2. 10 is a line for returning the liquefied propylene from the condenser 2 to the polymerization vessel 1, 11 and 12 are lines for extracting the slurry of the polyolefin (polypropylene) particles and liquefied propylene from the polymerization vessel and carrying them to the cyclone 7, and 13 is a line which returns the polyolefin (polypropylene) particles and liquefied propylene mixture to the polymerization vessel 1.

The operation of the process shown in Fig. 1 will be explained below.

The liquefied propylene passes through the line 8 and is fed into the polymerization vessel 1. The quantity of liquefied propylene fed is controlled so that the height of the liquid surface in the polymerization vessel 1 is constant. The principal catalyst, cocatalyst, and electron donor are fed beginning in the middle of line 8. The principal catalyst used may be, for example, a catalyst made by reacting a catalyst consisting of titanium chloride supported on magnesium with an organoaluminum compound, or a catalyst which has been treated by preliminary polymerization. As the cocatalyst, an organoaluminum compound can be used, and as the electron donor, various kinds of silane compounds can be used. The principal catalyst, cocatalyst, and electron donor may be fed continuously. The liquefied propylene fed from line 8 is polymerized in the polymerization vessel 1 and is concentrated in the liquefied propylene as polypropylene particles containing active catalyst, forming a slurry. On the other hand, some of the liquefied propylene in the slurry is gasified and removes the heat of polymerization produced in the polymerization vessel 1. Furthermore, the gasified propylene passes through line 9 as a mixed gas which contains hydrocarbon gases, such as propane, which are contained as impurities, and hydrogen, which was added as a molecular weight regulator; this mixed gas is carried to the condenser 2.

The mixed gas removed from the polymerization vessel 1 and passed through the line 9 is carried to the condenser, where the gasified

propylene is liquefied. This liquefied propylene passes through line 10 and is returned to the polymerization vessel 1. The quantity of the mixed gas returned to the condenser 2 is regulated by increasing and decreasing the opening of the flow rate regulating valve a. The internal pressure of the polymerization vessel, i.e., the polymerization temperature, is regulated by increasing and decreasing the quantity of the mixed gas carried to the condenser 2.

The slurry of polypropylene particles produced in the polymerization vessel 1 is extracted from the polymerization vessel 1 and passed through line 11; after this, it passes through line 12 and is fed to the cyclone 7. In the cyclone 7, the polypropylene particles in the slurry are divided into large-diameter and small-diameter particles. The small-diameter particles are recovered as a slurry from the upper part of the cyclone 6 and returned through line 13 to the polymerization vessel 1. The large-diameter particles, on the other hand, form a concentrated slurry and are expelled from the bottom of the cyclone 7 through the flow rate regulating valve b; they pass through line 15 and are sent to the solid-gas separator 3. The slurry concentration of the concentrated slurry can be increased and decreased by adjusting the flow rate regulating valves b and c. When the concentrated slurry is expelled from the flow rate regulating valve b, the liquefied propylene contained in it is immediately gasified and forms a mixture with the low-temperature gasified propylene and the large-diameter polypropylene particles. This mixture flows together with the recycled gas circulating in lines 16, 17, and 19 and is sent to the solid-gas separator 3. Furthermore, it is desirable to expel the concentrated slurry continuously.

The gasified propylene and polypropylene particles are separated in the solid-gas separator 3; the polypropylene particles are removed through line 20. If desired, the propylene particles which have been removed through line 20 can be sent through a process of demineralizing, a process of removing atactic polypropylene, a drying process, or a pelletizing process and recovered as the product. Furthermore, the polypropylene particles from line 20 may be fed into the next polymerization vessel; the same or a different monomer may be added to this polymerization vessel, and a second-stage polymerization may be performed. Examples of desirable monomers fed into this second-stage polymerization are 1 or more a-olefins selected from a group including ethylene, propylene, 1-butene, 1-pentene, 4-methylpentene-1, 1-hexene, and 1-octene.

On the other hand, the gasified propylene separated in the solid-gas separator 3 is circulated through lines 16, 17, and 19. Some of the gasified propylene is extracted through line 18 and sent to the monomer recovery process, not shown.

An example of applying the continuous production process of this invention to an actual polypropylene bulk polymerization will be shown below. The propylene used had a purity of 95 %, and the principal impurity was propane.

The properties of the polypropylene particles obtained were measured as described below. The particle diameter distribution, the melt flow rate, and the proportion of the isotactic portion were measured in the polypropylene particles before the demineralizing process, and the fish eyes, the Izod impact strength, and the appearance of the injection molded articles were measured in the polypropylene particles after the demineralizing process.

Particle diameter distribution: The polypropylene particles were classified by using sieves with meshes of 74 mm and 840 mm to obtain the proportions of polypropylene particles with diameters less than 74 mm and particles with diameters exceeding 840 mm.

Melt flow rate (MF): measured according to ASTM D1238.

Proportion of isotactic portion (HI): the polypropylene particles obtained were made into a film 0.1 mm thick by hot pressing; this film was cut into 1 cm squares, and the cut film was extracted for 6 hours in a Soxhlet extractor, using boiling normal heptane.

After this, the proportion of the insoluble fraction was measured.

Fish eyes: A film 25 mm thick was obtained by using a T die, after which the number of fish eyes in the film was counted with a Hutech Origine Co. fish eye counter; the number was expressed as the count per 450 cm².

Izod impact strength: measured according to ASTM D256.

External appearance of injection molded articles: The external appearances of the test pieces used in measuring the Izod impact strength were evaluated with the naked eye.

Working Example 1

An example of bulk polymerization of propylene is shown in the process of Fig. 1. In this working example, a 200-liter polymerization vessel equipped with a stirrer was used.

First, the method of preparing the principal catalyst will be described. Fifteen liters of normal heptane were charged into a 30-liter jacketed preliminary polymerization vessel equipped with a stirrer. While the temperature was kept at 10°C, 0.7 liter of a 15 wt % normal heptane solution of triethylaluminum (TEA) was charged into the vessel. Furthermore, 0.7 liter of a 1 mol/l normal heptane solution of t-butylethyl dimethoxsilane (TBEDMS) was charged into the vessel, and 500 g THC-32A catalyst (Toho Titanium Co.) was packed into it. This vessel was pressurized to 0.5 kg/cm² G with nitrogen gas. The THC-32A catalyst used in this case consisted of titanium chloride supported on modified magnesium chloride. Next, 500 g propylene gas were introduced into the preliminary polymerization vessel under pressure; at the time

it was introduced, the pressure was maintained at 2.0 kg/cm² G, but after 40 minutes the pressure became 0.5 kg/cm² and the preliminary polymerization was completed. The principal catalyst obtained was in slurry form; the solids concentration of this slurry was 61 g/l. This slurry was fed to the following polymerization reaction by feeding it into the polymerization vessel quantitatively.

Next, the polymerization will be explained. The polymerization was performed with a liquid quantity of 110 liters, using a jacketed 200-liter polymerization vessel equipped with a stirrer. As the cocatalyst, TEA was used, and as the electron donor, TBEDMS was used. The liquefied propylene which was used as the monomer was fed from line 8 in such a way that the height of the liquid surface in the polymerization vessel 1 was constant. The feed quantity of the propylene was 36,500 g/hr. The principal catalyst was fed into the polymerization vessel 1 at 0.5 g/hr, in terms of the THC-32A catalyst; the TEA and TBEDMS were fed at 6.4 g/hr and 1.5 g/hr, respectively, in terms of the pure products. The hydrogen gas used to regulate the molecular weight was fed into the polymerization vessel 1 in such a way that the melt flow rate of the polypropylene particles obtained by the polymerization was 80. The quantity fed at this time was 233 Nl/hr.

The polymerization was performed at 78°C.

The slurry formed was continuously extracted through line 11, placed at the bottom of the polymerization vessel 1, and sent to the cyclone 7 by the pump 6; there, it was separated into a slurry of large-diameter particles and a slurry of small-diameter particles. The slurry of the large-diameter particles was extracted from the bottom of the cyclone 7 as a concentrated slurry; the slurry of the small-diameter particles was extracted from the top of the cyclone 7 and returned to the polymerization vessel 1 through line 13. The concentrated slurry was sent through line 14; the flow rate regulating valve b was opened and closed intermittently, and the slurry was sent into line 5. The slurry concentration of the concentrated slurry was regulated at 55 wt % by adjusting the degree of opening of the flow rate regulating valve c. The liquefied propylene in this concentrated slurry was gasified at the outlet of the flow rate regulating valve b, and the concentrated slurry became a mixture of polypropylene particles and gasified propylene. The mixture leaving the flow rate regulating valve b was sent to the solid-gas separator (bag filter) 3, where it was separated into polypropylene particles and gasified propylene; the polypropylene particles were recovered as polypropylene powder. The quantity of polypropylene powder recovered per hour was 20.1 kg. Catalyst extraction and washing were performed on the recovered polypropylene powder in the mixed solution for demineralizing, and demineralizing was performed. The demineralizing was performed by first suspending the polypropylene

particles in a mixed solution so that the slurry concentration was 20 wt %. The catalyst in the polypropylene particles was extracted and removed at 85°C for 30 minutes; next, the mixed solution was blown on the polypropylene particles at 85°C to wash them. The catalyst extraction and washing were repeated twice. After the demineralizing, the polypropylene particles were dried for 12 hours at 60°C and under a pressure of 10 torr. On the other hand the gasified propylene which was separated in the solid-gas separator 3 passed through the compressor 4 and the heater 6 and was circulated in the circulating lines 16, 17, and 19; at the same time, part of it was extracted from line 18 so that the quantity circulating was constant.

The device could be operated in a stable manner. Moreover, the polypropylene obtained had a melt flow rate (MFR) of 80 and an isotactic structure proportion (HI) of 98.7%. The particle diameter distribution was as follows: the particles with diameters less than 74 mm comprised 1.0 wt % of the total particles and those with diameters larger than 840 mm comprised 25.5 wt %. The Izod impact strength was excellent, 5.5 kgf·cm/cm, and the number of fish eyes was only 6/450 cm². The surface state of the injection molded articles obtained was extremely smooth.

Working Example 2

The same operations were performed as in Working Example 1, except that the slurry concentration of the concentrated slurry was regulated at 60 wt %. The quantity of propylene fed in this case was 33,700 g/hr and the quantity of hydrogen fed was 203 Nl/hr. The quantity of polypropylene recovered per hour was 20.2 kg. The device could be operated in a stable manner. Moreover, the polypropylene obtained had a melt flow rate (MFR) of 80 and an isotactic structure proportion (HI) of 98.7%. The particle diameter distribution was as follows: the particles with diameters less than 74 mm comprised 0.7 wt % of the total particles and those with diameters larger than 840 mm comprised 26.0 wt %. The Izod impact strength was excellent, 6.0 kgf·cm/cm, and the number of fish eyes was only 4/450 cm². The surface state of the injection molded articles obtained was extremely smooth.

Working Example 3

The same operations were performed as in Working Example 1, except that the slurry concentration of the concentrated slurry was regulated at 65 wt %. The quantity of propylene fed in this case was 31,500 g/hr and the quantity of hydrogen fed was 178 Nl/hr. The quantity of polypropylene recovered per hour was 20.5 kg. The device could be operated in a stable manner. Moreover, the polypropylene obtained had a melt flow rate (MFR) of 80 and an isotactic structure proportion (HI) of 98.7%. The particle diameter distribution was as follows: the particles with diameters

less than 74 mm comprised 0.5 wt % of the total particles and those with diameters larger than 840 mm comprised 26.5 wt %. The Izod impact strength was excellent, 6.5 kgf·cm/cm, and the number of fish eyes was only 3/450 cm². The surface state of the injection molded articles obtained was extremely smooth.

Working Example 4

The same operations were performed as in Working Example 1, except that the slurry concentration of the concentrated slurry was regulated at 70 wt %. The quantity of propylene fed in this case was 30,000 g/hr and the quantity of hydrogen fed was 158 Nl/hr. The quantity of polypropylene recovered per hour was 21.0 kg. The device could be operated in a stable manner. Moreover, the polypropylene obtained had a melt flow rate (MFR) of 80 and an isotactic structure proportion (HI) of 98.8%. The particle diameter distribution was as follows: the particles with diameters less than 74 mm comprised 0.5 wt % of the total particles and those with diameters larger than 840 mm comprised 26.0 wt %. The Izod impact strength was excellent, 6.5 kgf·cm/cm, and the number of fish eyes was only 3/450 cm². The surface state of the injection molded articles obtained was extremely smooth.

Working Example 5

The same operations were performed as in Working Example 1, except that the slurry concentration of the concentrated slurry was regulated at 75 wt %. The quantity of propylene fed in this case was 25,300 g/hr and the quantity of hydrogen fed was 131 Nl/hr. The quantity of polypropylene recovered per hour was 19.0 kg. The device could be operated in a stable manner. Moreover, the polypropylene obtained had a melt flow rate (MFR) of 80 and an isotactic structure proportion (HI) of 98.8%. The particle diameter distribution was as follows: the particles with diameters less than 74 mm comprised 0.5 wt % of the total particles and those with diameters larger than 840 mm comprised 26.0 wt %. The Izod impact strength was excellent, 6.5 kgf·cm/cm, and the number of fish eyes was only 5/450 cm². The surface state of the injection molded articles obtained was smooth.

Comparison Example 1

Bulk polymerization of propylene was performed by the conventional process, shown in Fig. 2; the same operations were performed as in Working Example 1, except that the quantity of propylene fed to the polymerization vessel 1 was 40,000 g/hr. The quantity of polypropylene recovered per hour was 20.0 kg. The device could be operated in a stable manner. Moreover, the polypropylene obtained had a melt flow rate (MFR) of 80 and an isotactic structure proportion (HI) of 98.7%. The particle diameter distribution was as follows: the particles with diameters less than 74 mm comprised

3.0 wt % of the total particles and those with diameters larger than 840 μm comprised 25.0 wt %. The Izod impact strength was inferior, 4.5 kgf \cdot cm/cm, and the number of fish eyes was 15/450 cm^2 . The surface state of the injection molded articles obtained was good.

Table 1

Table 1

| | | Working Examples | | | | | Comparison Example |
|---------------------------|--|--|----------------|----------------|----------------|-------------------|--------------------|
| | | 1 | 2 | 3 | 4 | 5 | |
| Polymerization conditions | Temperature ($^{\circ}\text{C}$) | 78 | Same | Same | Same | Same | Same |
| | Quantity of solution (l) | 110 | Same | Same | Same | Same | Same |
| | Quantity of catalyst fed (g/hr) | 0.5 | Same | Same | Same | Same | Same |
| | Quantity of TEA fed (g/hr) | 6.4 | Same | Same | Same | Same | Same |
| | TBEDMS (g/hr) | 1.5 | Same | Same | Same | Same | Same |
| | Hydrogen (Nl/hr) | 233 | 203 | 178 | 158 | 131 | 269 |
| | Slurry concentration in polymerization vessel (wt %) | 50 | 50 | 50 | 50 | 50 | 50 |
| Results | Concentration of concentrated slurry (wt %) | 55 | 60 | 65 | 70 | 75 | 50 |
| | Quantity of propylene fed (kg/hr) | 36.5 | 33.7 | 31.5 | 30.0 | 25.8 | 40.0 |
| | Quantity of polymer recovered (kg/hr) | 20.1 | 20.2 | 20.5 | 21.0 | 19.0 | 20.0 |
| | Operating stability | Good | Good | Good | Good | Somewhat variable | Good |
| | MF (g/10 min) | 80 | 80 | 80 | 80 | 80 | 90 |
| | HI (%) | 98.7 | 98.7 | 98.7 | 98.8 | 98.8 | 98.7 |
| | Particle diameter distribution $<4 \mu\text{m}$ | 1.0 | 0.7 | 0.5 | 0.5 | 0.5 | 3.0 |
| | | 25.5 | 26.0 | 26.5 | 26.0 | 26.0 | 25.0 |
| | | >840 μm | | | | | |
| | | Number of fish eyes | 6 | 4 | 3 | 3 | 5 |
| | | Izod impact strength | 5.5 | 6.0 | 6.5 | 6.5 | 4.5 |
| | | External appearance of injection-molded articles | Extremely good | Extremely good | Extremely good | Extremely good | Good |

Brief Explanation of Drawings

Fig. 1: Process diagram, showing an example of the application of the continuous production process of this invention to the bulk

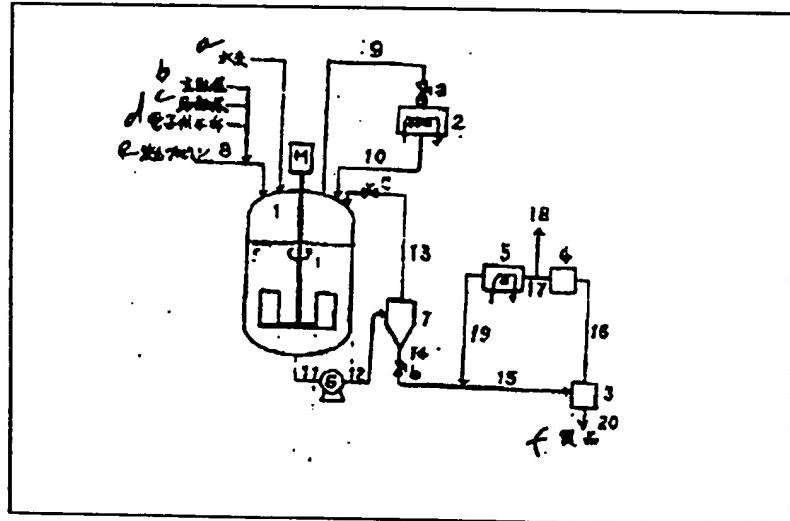
Polymerization of polypropylene

Fig. 2: Process diagram, showing the conventional process of the bulk polymerization of polypropylene

Explanation of Symbols:

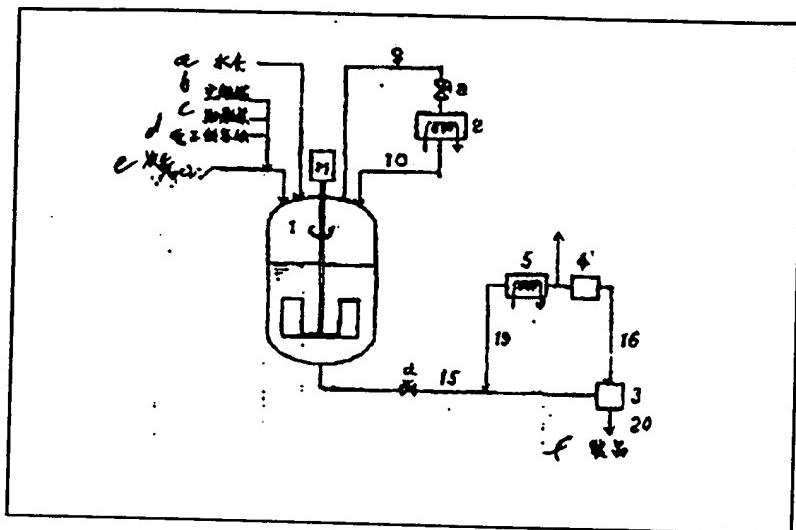
- 1 ... Polymerization vessel
2 ... Condenser
3 ... Solid-gas separator
4 ... Compressor
5 ... Heater
6 ... Pump
7 ... Cyclone
8 ... Line for feeding liquefied propylene to polymerization vessel 1
9 ... Line for carrying mixed gas from polymerization vessel 1 to condenser 2
10 ... Line for returning liquefied propylene from condenser 2 to polymerization vessel 1
11 and 12 ... Lines extracting slurry of polyolefin (polypropylene) particles and liquefied propylene from polymerization vessel and carrying it to cyclone 7
13 ... Line for returning slurry of polyolefin (polypropylene) particles and liquefied propylene to polymerization vessel 1

Fig. 1



- a. Hydrogen d. Electron donor
 - b. Principal catalyst e. Liquefied polypropylene
 - c. Cocatalyst f. Product

Fig. 2



- a. Hydrogen d. Electron donor
 - b. Principal catalyst e. Liquefied polypropylene
 - c. Cocatalyst f. Product

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